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NORTH URAL APOVULCANITES AS RAW MATERIAL FOR PORCELAIN PRODUCTION

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The apovulcanites from the Republic of Komi which are analogues of porcelain rocks are studied as a material of the quartz-feldspar type for electrotechnical, household, and sanitary ware ceramics. The effect of kaolinite clay and low-iron Timanskii bauxite on the production conditions, the structure, and the properties of apovulcanite-based ceramics is investigated. It is shown that apovulcanite can be used in production of porcelain articles.

In Russia there are several prospected deposits of porcelain rocks, and two geological provinces (Sikhote-Alin' and Caucasus) are currently considered in the context of their subsequent industrial use [1]. Until recently, the Ural region was not regarded as promising with respect to porcelain rock deposits. However, as a consequence of long-term explorations, some porcelain rock deposits were discovered in the north of the region, which made it possible to put forward and substantiate an assumption that the rest of the Ural region as well is promising for mining of this raw material.

Analogues of porcelain rocks were identified among the metasomatically modified varieties of trachyliparites which are present here in the widely occurring late-Cambrian and early-Paleozoic vulcanogenic strata. According to a preliminary estimate, the resources of porcelain rocks can be evaluated as follows: about 80 million m^3 within the limits of the Kapkanvozhskii site, 1000 million m^3 in the region of the Paipudynskii liparite rock mass, and about 3 million m^3 in the region of the Sivyaga River. Substantial resources, surface bedding (strip mining is possible), and the accessibility of railroads increase the economic expedience of mining of this material.

The petrographic analysis of the porcelain rocks revealed that apovulcanite silicates have a leucocratic composition with total absence of chromatic minerals. The rock consists of orthophyric and felsite quartz-feldspar basic mass, and on this background inclusions of potash feldspar and albite, and secondary and accessory minerals are found as well: sericite, calcite, sphene, typomorphic rutile, clinoclase orthite, sirlesite, turmaline, less often, zircon, etc. [3]. According to spectral analysis data, apovulcanites contain microimpurities of Be, Pb, Ga, V, Ba, Mn, Sc, and some other elements.

Based on the results of the petrographic and chemical analysis, it was established that the acid apovulcanites from the Northern Ural by their composition can be divided into two main types: dense and schistose close-grained light-colored rocks of white, yellowish and bluish tints, often with a well preserved quartz-porphyry structure with sericite-quartz or pyrophyllite-sericite-quartz composition (the Kapkanvozhskii type of porcelain rock), and fine-grained rocks of bluish-greenish-gray and light-creamy colors with nearly monomineral potash feldspar composition, containing insignificant quantities of quartz and sericite (Sivyaginskii type of porcelain rock).

Table 1 shows the averaged chemical and mineral composition of the two varieties of porcelain rocks from the Northern Ural. As a result of the qualitative x-ray phase and petrographic analysis and calculation of the mineral composition of the rocks based on their chemical composition, differences in the phase compositions of the considered apovulcanites were identified. Both types of rocks resemble the raw material from the Gusevskii and Sergeevskii deposits in their content of the basic components.

According to the classification proposed in [1, 4, 5] and based on the content of the main mineral phases, the material of the Kapkanvozhskii type can be attributed to the sericite(muscovite)-quartz type, and the Sivyaginskii type of material can be related to the feldspar-quartz type.

The chemical composition of the North Ural rocks differs from the porcelain rocks from other deposits by an increased content of iron and titanium oxides and a high potash modulus. The mineral composition is characterized by an increased content of quartz and the absence of kaolinite.

The main components of the material are SiO_2, Al_2O_3, and $Na_2O + K_2O$. The total content of these components in the rocks comprises 94 – 98 wt.%. The limits of the concentration of each component significantly vary over different sites (%): 72 – 80 SiO_2, 12 – 17 Al_2O_3, 1.0 – 6.5 $Na_2O_3 + K_2O$. Comparing the composition of the considered material with the typical averaged composition of the mixture for electrotechnical porcelain, it should be noted that both types of material are distinguished by a slightly increased content of quartz, pigment oxides, fluxes, and a decreased content of aluminum oxide.

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TABLE 1

Material	Chemical composition, wt.%							Mineral composition, vol.%
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3 + FeO	CaO	K_2O	Na_2O	
Porcelain rock:								
Kapkanvozhskii	74.28	16.31	0.33	1.04	0.24	4.32	0.54	60 quartz, 20 sericite, 20 argillaceous components
Sivyaginskii	77.75	11.30	–	1.05	0.30	6.60	1.80	25 quartz, 40 microcline, 35 albite
Gusevskii	76.26	16.80	0.19	0.30	0.15	0.11	0.75	55 quartz, 30 – 40 kaolinite, 15 muscovite
Standard mixture for hard porcelain	62.00	22.00	0.50	–	1.00	0.50	0.20	50 kaolinite, 25 quartz, 25 feldspar
Veselovskaya clay	53.00	> 33.00	< 1.50	< 1.00	< 1.10	1.50	1.50	63 kaolinite, 20 hydromica, 17 quartz
Timanskii low-iron bauxite	9.87	69.23	3.78	1.53	0.06	0.87	0.10	90 boehmite, 8 kaolinite, 2 rutile

Among the components limiting the quality of the material are iron oxides whose total content should not exceed 0.5 – 1.0%. The content of iron oxides at different sites of the bed varies from 0.08 to 1.41%. The possibility of removing iron oxides by the magnetic separation method was investigated in principle, and some positive results were obtained in extraction of pigment oxides whose content after separation decreased by a factor of 1.5 – 2 [2].

Thus, the results of the chemical, phase, petrographic and spectral analysis suggest the following: the North Ural apovulcanites by their quality and composition represent a valuable material of the quartz-feldspar type, resembling in composition the porcelain rocks of known deposits such as Gusevskii, Sergeevskii (seaside region) and the Kishkitskii deposit (North Caucasus) [5].

The possibility of using apovulcanites from the Northern Urals in their natural state and after separation as a basic complex component for porcelain production was thoroughly investigated [3, 6]. The experimental porcelain samples were prepared by the standard technology: preliminary crushing of the rock, wet grinding to passing through a No. 006 sieve, introduction of alumina-bearing additives in the phase of grinding, molding of articles using the semidry compression method with carbomethylcellulose binder, compression in molds at a pressure of ≅ 40 MPa. The samples were sintered in electric furnaces in the temperature interval of 1100 – 1250°C for 0 – 6 h and the rate of the temperature rise was 300°C/h.

The qualitative changes in the phase composition of a sample in sintering were determined by the results of x-ray phase analysis. The quantitative ratio of the oxide phases in the sample were found by x-ray phase analysis using the traditional method [7] with CaF_2 as the internal reference standard. The optimum temperature and duration of firing were determined based on the change in the values of water absorption, linear shrinkage, apparent density, and open porosity. The microstructure of the sintered material was studied with an electron microscope both in transmitted and reflected light.

It was found that the samples made of Sivyaginskii-type material in firing produce only one crystal phase, namely, quartz, whose part by volume attains 40%. The samples made of Kapkanvozhskii-type material in firing produce two crystal phases: quartz and mullite, whose ratio is determined by the temperature and duration of firing. The emergence of the mullite phase in the material is determined by the presence of a small quantity of kaolinite in the initial material, which in decomposition produces primary mullite crystals which grow with an increase in the temperature and duration of firing.

The optical microscopic analysis of the microstructure of the sintered samples revealed the following elements in the samples based on the Kapkanvozhskii material: fused quartz grains about 30 μm in size, needle-shaped mullite crystals up to 8 – 10 μm long, and single rounded pores which are uniformly distributed over the bulk of the vitreous phase. Accordingly, judging from the phase composition and the microstructure of this material, it can be classified as porcelain. The microstructure of the sample of the Sivyaginskii material is represented by quartz crystals of various sizes and single rounded pores uniformly distributed over the bulk of the vitreous phase, which makes it possible to regard this material as glass ceramics.

The phase composition and main physicomechanical properties of the ceramic materials obtained from porcelain rocks at the optimum conditions are shown in Tables 2 and 3.

As can be seen, the electric properties and mechanical strength of the obtained materials meet the requirements placed upon engineering porcelain. Significant disadvantages of these materials include, first, a dark color of fracture caused by partial reduction of titanium dioxide in firing, and, second, the low thermal stability of the material due to the high total content of alkali metal oxides and high potash modulus.

Introduction of alumina-containing components such as kaolinite clay or bauxites into the molding mixture in the stage of its preparation improves the microstructure of the material, increases its strength, heat resistance, and whiteness due to an increase in the content of the mullite phase and a decrease in the concentration of iron and titanium oxides. Clay from the Veselovskoe deposit and Timanskii low-iron bauxite (Table 1) were used as alumina-containing additives. The effect of the mineral type of the additive on the sintering state interval and the physicotechnical and strength

TABLE 2

Type of material	Phase composition, vol.%		
	quartz	mullite	glass phase
Kapkanvozhskii	20 – 30	10 – 15	55 – 60
Sivyaginskii	20 – 30	–	70 – 80

TABLE 3

Parameter	Samples based on	
	Kapkanvozhskii material	Sivyaginskii material
Sintering temperature, °C	1180 – 1250	1140 – 1200
Sintering interval, °C	70	60
Apparent density, g/cm^3	2.35 – 2.40	2.30 – 2.35
Water absorption, %	0.1 – 3.0	0.1 – 7.0
Bending strength, MPa	70 – 90	50 – 70
Dielectric constant at 20°C	7 – 8	7 – 8
Dielectric loss tangent at frequency of 1 kHz and temperature of 20°C	1.0 – 2.0	1.0 – 4.0
Electric strength at frequency of 20 Hz, kW · mm	29	30

properties of the modified material were studied on samples obtained from the Kapkanvozhskii type of raw material containing 20 to 50 wt.% clay or bauxite. The firing conditions remained constant: firing was performed at the temperature of 1200°C for 1 – 3 h. The mixture compositions and the physicomechanical properties of the samples with natural additives are given in Tables 4 and 5.

The material modified with the additives exhibits improved molding capacity, a wider interval of the sintered state, less intense fracture pigmentation, and increased strength of the samples. No qualitative changes in the phase composition of the ceramic were observed on introducing the additives, and the quantitative content of mullite increased to 23 – 25 vol.% in the samples produced under the optimum conditions: firing temperature of 1200 – 1250°C and firing duration of 1 – 3 h. If the specified temperature interval or firing duration are exceeded, the content of mullite in the material significantly decreases due to its dissolution in the liquid phase. As a consequence, the strength of the samples obtained at a temperature above 1280°C or with a firing duration exceeding 3 h is 20 – 30% lower, compared to the samples obtained in the optimum conditions.

The electron microscopic study of the microstructure of the samples with natural additives obtained in the optimum conditions did not reveal any significant alterations. The microstructure of the ceramic samples with natural additives is similar to that of the initial apovulcanites without additives, i.e., it consists of fused quartz grains 20 – 30 μm in size, needle-shaped mullite crystals 8 – 10 μm long, single round-shaped pores 10 – 15 μm in size, and occasional inclusions of the gas phase which are uniformly distributed in the glass phase.

TABLE 4

Sample	Mixture composition, wt.%		
	Kapkanvozhskii porcelain rock	Veselovskoe clay	Timanskii low-iron bauxite
1	50	50	–
2	60	40	–
3	70	30	–
4	80	20	–
5	50	–	50

TABLE 5

Sample	Water absorption, %	Linear shrinkage, %	Apparent density, g/cm^3	Open porosity, %	Bending strength, MPa
1	0.0 – 0.2	10.0	2.52	0.0 – 0.2	70 – 80
2	0.2 – 0.5	9.0	2.48	0.5 – 1.0	65 – 75
3	0.2 – 0.5	9.0	2.49	0.5 – 1.0	60 – 70
4	0.5 – 1.2	9.0	2.46	0.5 – 1.0	50 – 60
5	0.0 – 0.2	5.0	2.53	0.0 – 0.2	80 – 90

Thus, apovulcanites, i.e.,, the porcelain rocks from the Republic of Komi, are valuables materials of the quartz-feldspar type which can be used in production of electrical engineering, household, and sanitary porcelain materials. Modification of ceramic mixture compositions with additives of kaolinite clay and low-iron presintered bauxite from the Timanskii deposit substantially improves the mechanical and structural properties of the material. This makes it possible to expand the potential application areas.

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